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(54) Carbon dioxide gas lasers

(57) A carbon dioxide laser comprises an envelope 1 containing an electrode structure 2, 3, and reflecting and partially reflecting mirrors 10, 11. A tin (IV) oxide-supported palladium or

platinum catalyst contained in porous structures 22 of alumina or silica is mounted inside the envelope to provide a room temperature catalytic oxidation of CO during and following discharge of the laser in a pulsed or continuous wave mode of operation.

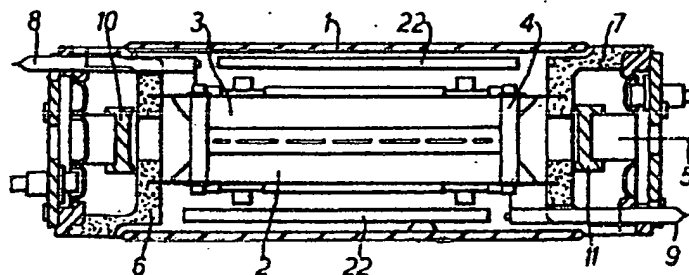


Fig. 2

The drawings originally filed were informal and the print here reproduced is taken from a later filed formal copy.

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## SPECIFICATION

## Carbon dioxide gas lasers

This invention relates to carbon dioxide ( $\text{CO}_2$ ) gas lasers in which laser emission is initiated by electrical discharge within an envelope containing the gas.

A typical  $\text{CO}_2$  laser comprises an envelope or tube containing a gas mixture e.g. of  $\text{CO}_2$ ,  $\text{N}_2$ , and He, electrodes for providing an electrical discharge within the gas, a reflecting and a partially reflecting mirror spaced apart and often parallel to one another at opposite ends of the envelope.

Lasers can be divided into two groups, continuous wave (CW) and pulsed lasers; the former emits radiation continuously (when supplied with power) whilst the latter emits radiation in short bursts. Both groups may use a flowing gas system or a sealed envelope system.

The electrical discharge in the gas causes a dissociation of  $\text{CO}_2$  into CO and  $\text{O}_2$ . In the flowing gas system the reaction gas products are swept out of the envelope but in the sealed system these products remain within the envelope and, unless recombined into  $\text{CO}_2$ , result in loss of output, for example by causing arcing between the electrodes with possible consequential failure of the laser.

In general the difficulties caused by  $\text{CO}_2$  dissociation increases in severity as the pressure of the active gas is raised. Thus CW lasers which operate at e.g. 20 Torr. do not have the problem to the same extent as pulsed lasers operating at atmospheric pressure. At higher gas pressures transverse (of the laser axis) excitation of the discharge is normally used, these are termed TE lasers. Lasers operating at atmospheric gas pressure with transverse excitation are termed TEA (transverse excitation atmospheric pressure) lasers. With these higher pressure gas lasers the presence of the dissociation products CO and  $\text{O}_2$  tends to cause the uniform electrical discharge to degrade into localised arcs with consequential dramatic loss of performance.

One form of TEA laser uses a trigger wire to produce subsidiary discharges to the anode causing ultra violet irradiation of the cathode. This produces the diffuse photo emission of electrons necessary for the creation of a uniform discharge and helps counter the arcing problem. Such a laser is described in IEEE Journal of Quantum Electronics, Vol. QE11, No. 9, September 1975, pages 774-778.

Another TEA laser is described in J. Phys. E Sci. Instruments, Vol. 11, 1978, pages 311-315. It uses two arrays of sliding arcs to provide ultra violet radiation which pre-ionises the gas between the principal electrodes of the laser before high volts are applied to these, thus encouraging the formation of a uniform discharge. Additionally a heated platinum wire is used to catalyse the recombination of CO and  $\text{O}_2$ . Use of a Pt wire in a  $\text{CO}_2$  TEA laser is described in J. Phys. E Sci. Instrum., Vol. 11, 1978, pages 316-319. A disadvantage of such a heated wire is its power consumption, typically about 8 watt, which adds

to the required battery weight in portable equipment and may result in thermal distortion of the laser envelope.

According to this invention a carbon dioxide gas laser comprises an envelope containing a gas including carbon dioxide, a structure for inducing an electric discharge within the envelope, a reflecting and a partially reflecting mirror spaced apart and a catalyst material for recombining carbon monoxide and oxygen into carbon dioxide, the catalyst being either tin (IV) oxide-supported palladium or tin (IV) oxide-supported platinum.

The structure for inducing an electric discharge may be spaced electrodes, or radio frequency induction.

The catalyst may be incorporated into porous structures such as activated alumina, silica etc., and be formed into strips or sheets. The amount of Pd or Pt within or on the  $\text{SnO}_2$  may vary, a typical value is around 2% by weight. The catalyst operates unheated at ambient temperatures even in very cold climates, but it may include a small power consumption heater for initial use until the laser envelope reaches its operating temperature.

The laser may be a CW or a pulsed laser with a sealed envelope or an unsealed envelope. The laser may include a device such as a fan to circulate the laser gas.

The use of tin (IV) oxide-supported palladium has previously been suggested for use in automobile exhaust systems, G. Croft and M. J. Fuller, Nature, Vol. 269, 13 October 1977, page 585/6. However automobile exhaust systems operate at elevated temperatures and it has previously been considered necessary to use such high temperatures for catalytic oxidation of CO by  $\text{O}_2$  and  $\text{N}_2$ . In addition catalytic exhaust systems operate with considerable excess air rather than stoichiometric amounts of CO and  $\text{O}_2$ .

The invention will now be described, by way of example only, with reference to the accompanying drawings of which:-

Figure 1, 2 are plan and side sectional views of a transversely excited atmospheric pressure  $\text{CO}_2$  laser;

Figure 3 is a circuit diagram for the laser of Figure 1.

As shown in the drawings a laser comprises an envelope 1 made of glass and expansion matched Ni-Fe-Co alloy. The envelope 1 is filled with gas at 760 Torr. pressure and a composition by volume of 40%  $\text{CO}_2$ , 20%  $\text{N}_2$ , 40% He. Two Rogowski-profiled nickel electrodes 2,3 are spaced apart by alumina spacers 4 parallel to the laser axis 5. These electrodes 2,3 are supported by alumina blocks 6,7 which also carry electrical connections 8, 9 to the exterior of the envelope 1. At one end of the envelope 1 is a gold plated fully reflecting mirror 10 arranged normal to the laser axis 5 whilst at the other end of the envelope 1 is a multilayer-dielectric-coated germanium 85% reflection mirror 11 also arranged normal to the laser axis 5. At both sides of the envelope are rows of tee shaped tungsten rods 12, 13 which pass into the envelope 1 in a gas tight manner. The



pointed inner ends of the rods are spaced apart e.g. by 2mm arc gaps. Each row of rods 12,13 is connected to earth via capacitors 14,15 e.g. 4 pF capacitors, and the rows connected in parallel as shown in Figure 3. The energy for the arcs is provided by two 900pF 16, 17 capacitors charged to 30kV by an HT circuit 18 and connected via a triggered spark gap SG1. The energy for the electrodes 3, 4 is provided by a 10nF capacitor 19 also charged to 30kV by a HT circuit 20 and connected via a spark gap SG2. A delay 21, e.g. 2µs, allows sequential firing of SG1 and SG2.

Strips 22 of porous alumina incorporating 1.8% Pd-SnO<sub>2</sub> (or 1.3% Pt-SnO<sub>2</sub>) are mounted inside the envelope. Alternatively catalyst coated strips or rods may be mounted in the envelope. The (Pd-SnO<sub>2</sub>) catalyst may be prepared by standard processes e.g. by impregnating SnO<sub>2</sub> gel with H<sub>2</sub>PdCl<sub>4</sub> solution or cation-exchanging with Pd(NH<sub>3</sub>)<sub>4</sub>(OH)<sub>2</sub>, or by co-precipitating Pd(OH)<sub>2</sub> and hydrated SnO<sub>2</sub> from chloride solution with KOH followed by washing, drying, and re-washing. This results in SnO<sub>2</sub> particles supporting Pd in and/or on the surface. Such processes have been developed by the Tin Research Institute and described by G. C. Bond, L. R. Molloy and M. J. Fuller, J. Chem. Soc. (Chem. Communications) pages 796/7, 1975. These processes result in a tin (IV) oxide-supported palladium which is a more effective catalyst for the oxidation of CO than either SnO<sub>2</sub> or Pd is individually, particularly at low temperatures. Similarly, the Pt-SnO<sub>2</sub> catalyst may be prepared by standard processes e.g. by ion-exchanging a platinum chloride-ammonia complex (H<sub>2</sub>PtCl<sub>6</sub>+NH<sub>3</sub>) with SnO<sub>2</sub> gel, followed by reduction. This results in SnO<sub>2</sub> particles supporting Pt in and/or near the surface. Such processes have been developed by the Tin Research Institute.

These processes result in a tin (IV) oxide-supported platinum which is a more effective catalyst for the oxidation of CO than either SnO<sub>2</sub> or Pt is individually, particularly at low temperature.

The catalyst may be incorporated into porous structures by standard processes as described for example in R. L. Moss, *Experimental Methods in Catalytic Research*, Vol. 2, pages 43—94, Academic Press Inc. 1976.

In operation the spark gap SG1 is closed which results in a series of arcs being formed in sequence along the two rows of rods 12, 13. This provides pre-ionising ultra-violet radiation into the gas between the main electrodes 3, 4. After about 2µs (depending on the gas composition) the spark gap SG2 is closed resulting in the main electrical discharge and a consequential burst of laser radiation through the mirror 11. As a result some

CO<sub>2</sub> dissociates into CO and O<sub>2</sub>. The catalyst assists in the recombination of CO and O<sub>2</sub> into CO<sub>2</sub>. The amount of catalyst needed depends on the laser pulse repetition frequency (PRF) (and hence generation of O<sub>2</sub>) the acceptable degradation in laser performance (increasing O<sub>2</sub> concentration reduces performance), the temperature of the catalyst and its availability to the CO and O<sub>2</sub>. For a given pulse repetition frequency and permitted O<sub>2</sub> concentration the amount of catalyst must be increased until recombination matches dissociation. The rate of re-combination varies with temperature. It has been found for example, that O<sub>2</sub> and CO are removed by SnO<sub>2</sub>Pd from an initial mixture of 34% CO<sub>2</sub>, 20% N<sub>2</sub>, 40% He, 4% CO and 2% O<sub>2</sub>, at a rate of about 0.005 cm<sup>3</sup>/s/g per unit mass of catalyst at -30°C and 0.3 cm<sup>3</sup>/s/g at 40°C with a logarithmic relation at intermediate temperatures. In similar conditions, it has been found that O<sub>2</sub> and CO are removed by SnO<sub>2</sub>Pt at a rate of about 0.06 cm<sup>3</sup>/s/g at 17°C. This shows that the catalysts can operate at ambient temperatures even in very cold climates.

Use of SnO<sub>2</sub>-Pd or SnO<sub>2</sub>-Pt as catalysts is not limited to TEA lasers since they can be used with other CO<sub>2</sub> gas lasers to increase useful life times. For example they can be used with low pressure 20 Torr. CW lasers and CW waveguide lasers (gas pressure about 100 Torr.).

#### CLAIMS

1. A carbon dioxide laser comprising an envelope containing a gas including carbon dioxide, a structure for inducing an electric discharge within the envelope a reflecting mirror and a partially reflecting mirror characterised by a catalyst material of tin (IV) oxide-supported palladium or tin (IV) oxide-supported platinum.

2. A laser according to claim 1 wherein the catalyst is incorporated into a porous structure of alumina or silicon.

3. A laser according to claim 1 wherein the catalyst is coated onto rods or strips.

4. A laser according to claim 1 wherein the envelope is a closed envelope.

5. A laser according to claim 1 wherein the structure for inducing an electric discharge includes electrodes for causing a transverse excitation of the gas.

6. A laser according to claim 5 wherein electrode structures having arc gaps are provided for causing pre-ionisation of the gas.

7. A laser constructed, arranged and adapted to operate substantially as hereinbefore described with reference to the accompanying drawings.